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ON THE CALCULATION OF RELAXATION TIMES

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Chau, Le Fevre and Tardif[1] have suggested an empirical equation to calculate the relaxation times of polar molecules in dilute solution in non-polar solvents. From the known physical properties of the solute and solvent they have calculated the relaxation times for a number of polar molecules in different solvents using the equation

$$\tau = \pi\eta_1(\exp \Delta_1)ABC/2(\epsilon_1+2)kT \qquad \ldots \quad (1)$$

where η_1, Δ_1 and ϵ_1 are the viscosity, depolarisation factor observed in Rayleigh scattering and the dielectric constant of the non-polar solvent, while ABC are the dimensions pertaining to the solute molecule. They have compared the calculated relaxation times with their observed values and found reasonable agreement.

Another empirical equation namely,

$$\tau = 6\pi\eta_1\alpha/(\epsilon_1+2)kT \qquad \ldots \quad (2)$$

is now suggested in which η_1 and ϵ_1 are the viscosity and dielectric constant of the solvent and α is the polarisability of the solute molecule. This equation avoids the necessity of knowing Δ_1 and ABC, the quantities which cannot be easily obtained. α can be easily computed from a knowledge of the refractivity of the solute molecule.

The relaxation times calculated using equations (1) and (2) are given in the following table together with the observed values as given in reference (1). The data necessary for the calculation have been taken from (Chau *etal*, 1957).

An examination of the table shows that equation (2) in its simpler from gives equally satisfactory values for relaxation times as equation (1). The equation (2) has been tested for a number of other solutes and is found to give reasonable values for τ. Full details will be published elsewhere.

TABLE I

Solute	Solvent	$\tau_{eq(1)}$	$\tau_{eq(2)}$	$\tau_{obs} \times 10^{12}$ SeC.
Nitrobenzene	CCl_4	13	14	13–20
	C_6H_6	13	9.0	11–15
Nitronaphthalene	CCl_4	19	21	25
	C_6H_6	18	14	20
Nitroanthracene	CCl_4	24	30	23
	C_6H_6	23	20	28
Pyridine	CCl_4	20	9.6	7.2
	C_6H_6	10	6.3	4.4
Quinoline	CCl_4	15	16	14
	C_6H_6	14	11	10
iso-Quinoline	CCl_4	16	17	21
	C_6H_6	14	11	15
Acridine	CCl_4	19	24	26
	C_6H_6	18	16	20
4–Nitrodiphenyl	CCl_4	20	23	21
	C_6H_6	20	15	30

REFERENCE

Chau, J. Y. H., Le Fevre, R. J. W., and Tardif, J., 1957, *J. Chem. Soc.*, 2293.